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Evaluation of the Utility, Comparability, and Cost Effectiveness of Passive Groundwater Sampling Technologies When Compared to a Low-Flow Purging Method

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Background

- Regulators require expensive chemical analyses of groundwater samples by off-site environmental testing laboratories to characterize, clean up, and monitor contaminated/remediated sites.
- Passive sampling technologies may reduce costs when compared to traditional purging methods.
 - Reduce sampling time
 - Eliminate costs for disposal of purge water
 - Reduce capital equipment cost

Objective

- Demonstrate/validate (dem/val) the ability of alternative passive sampling technologies to provide technically defensible analytical data for chemical contaminants of concern to the Army and the Department of Defense (DoD)
 - Explosives
 - Polynuclear Aromatic Hydrocarbons (PAHs)
- Evaluate the utility, comparability, and cost effectiveness of sampling with these technologies as compared to the United States (U.S.) Environmental Protection Agency (EPA) low-flow purging method

Baseline – U.S. EPA Low Flow Purge Sampling Method

- Water in the well casing is non-representative of formation water.
- Purging is required because placing the sampling device in the well causes:
 - Mixing overlying stagnant casing water with waters in the screened interval
 - Disturbances of suspended sediment collected in the bottom of the casing
 - Displacement of water into the formation adjacent to the well screen
- Isolation of the screened interval water be accomplished using low-flow minimal drawdown techniques.
- Low flow purging minimizes mixing and disturbances of water within the casing/screened interval.
 - Pump intake is located within the screened interval, water pumped will be drawn in directly from the formation with little mixing of casing water or disturbance to the sampling zone
- A low pumping rate is maintained to purge the well until water quality indicator parameters such as pH, SC, DO, temperature, and turbidity stabilize.
 - Parameters are used to determine when formation water is accessed during purging.

(Puls, R. and Barcelona, J., 1996)

Baseline – U.S. EPA Low Flow Purge Sampling Method (Cont'd)

- Advantages

- Samples represent the mobile load of contaminants present (dissolved and colloid-associated)
- Minimal disturbance minimizes sampling artifacts
- Minimal operator variability, greater operator control

- Disadvantages

- High initial capital costs
- Extensive set-up time in the field
- Need to transport a lot of equipment to and from the site
- Labor intensive

(Puls, R. and Barcelona, J., 1996)

Alternative Sampling Technologies - Snap Sampler™

- Method which uses specialized equipment designed to minimize the impact the sampling process has on groundwater chemistry.
- Accomplished through deployment and passive re-equilibration of the monitoring well to ambient groundwater flow and diffusive contaminant flux within the well/aquifer system.
- Eliminates well purging prior to sample collection.
- Concept developed from past research that demonstrates most wells exhibit ambient flow-through under natural groundwater gradients.
 - Screen sections are “naturally purged” without pumping.
 - Natural ambient flow can induce mixing within wells, resulting in a flow-weighted averaging effect in the well without purging.
 - Many wells show relatively narrow ranges of vertical concentrations when vertically profiled.
- Snap Sampler takes advantage of “naturally purged” wells by capturing natural flow-through in the open bottle during sampler deployment.

(ProHydro, Inc., 2005)

Alternative Sampling Technologies – Snap Sampler (Cont'd)

- Utilizes a patented device that employs a unique double-end-opening bottle
- Can collect samples for various contaminants including volatile and semi-volatile organic compounds, pesticides, polychlorinated biphenyls (PCBs), metals, and other inorganic compounds, including perchlorate
- Designed to collect a whole water sample from a user-defined interval within the well screen without mixing fluid from other intervals.
 - No draw down, minimal agitation or displacement of water column

(ProHydro, Inc., 2005)



Double-End-Opening Bottle



Snap Sampler Equipment
(ProHydro, Inc.)



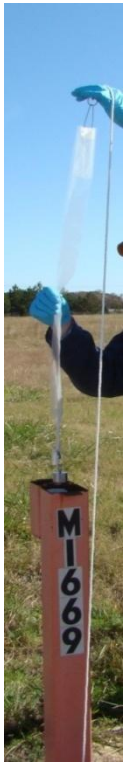
Deployment

Alternative Sampling Technologies – HydraSleeve

- Can be used to collect a representative sample for most physical and chemical parameters without purging the well
- Collects a whole water sample from a user-defined interval (typically within the well screen), without mixing fluid from other intervals
- Placed within the screened interval and when activated for sample collection, collects a sample with no drawdown of the water
 - Once the sampler is full, the one-way reed valve collapses, preventing mixing of extraneous, non-representative fluid during recovery.
 - *Must have an adequate water column (1.5 times length of sampler) in the screened interval above the sampler to completely fill Hydrasleeve or it will continue to fill with water from upper casing.

(GeoInsight, 2006)

Alternative Sampling Technologies – HydraSleeve (Cont'd)



***Deployment (Right) and
Retrieval (Left) of the
HydraSleeve Sampling
Technology***



Sample Transfer

Alternative Sampling Technologies - *In Situ* Tubular Extraction Device (InSTED)

- Developed by the Environmental Chemistry Branch-Omaha of the Engineer Research and Development Center (ERDC)
- Designed for the *in situ* extraction of explosive residues from groundwater in wells no less than 2 inches in diameter
- Also applicable to sampling pesticides, PAHs, polychlorinated biphenyls, and other semi-volatile analytes
 - Appropriate modifications to the cartridge selection and laboratory procedures are required.

(USACE, 2006)

Alternative Sampling Technologies - InSTED (Cont'd)

- **Method Summary**

- Cartridges are conditioned in the laboratory prior to use in the field; InSTED (modified HydraSleeve) is inserted in the well to the desired sample depth.
- After a 24-hour equilibration time, a discrete sample is taken.
- With the InSTED still in the well, the pump is turned on and operated until the sample passes completely through the device, approximately 30 minutes.
 - Technology is not mature for *in situ* extraction
 - Extraction is completed at surface.
- InSTED is then brought to the surface and cartridge is removed.
- Used cartridge is sealed in a plastic bag and kept in the dark for shipment to the analytical laboratory.

(USACE, 2006)

Alternative Sampling Technologies - *In Situ* Tubular Extraction Device (InSTED)

- Modified HydraSleeve with a bottom discharge, coupled with a Solid Phase Extraction (SPE) sampling cartridge.
 - InSTED modifies the HydraSleeve process so that it can be used to extract the analytes in the field.
 - Eliminates the need to maintain/ship large volumes of water.



***Bottom-Discharging Port
Added to Modified
HydraSleeve***



InSTED Sampler



InSTED SPE Extraction



SPE Cartridge

Technical Approach

- Demonstrate the alternative groundwater sampling technologies at two sites
 - Explosives
 - PAHs
- Analyze samples using conventional laboratory analyses for explosives (EPA 8330B) and PAHs (EPA 8270 SIM mode)
- Evaluate technologies based on the following criteria:
 - Providing technically defensible analytical data
 - Use with various contaminants
 - Required labor, equipment, and shipping costs
 - Ease of use and ruggedness/reliability
 - Time required to collect samples
 - Performance under varied well conditions

Demonstration 1

Milan Army Ammunition Plant (MLAAP)

- Demonstrated the technologies for use with explosives (MLAAP Nov 09):
 - Sampled 10 wells with the Snap Sampler, HydraSleeve, and InSTED
 - Sampled 5 wells with the U.S. EPA method (field conditions delayed schedule and made wells inaccessible)
- Analyzed samples using U.S. EPA Method 8330B.



Sampling with Alternative Technologies



Sampling with U.S. EPA Method

Demonstration 1 MLAAP – Results

- Analytical
 - Detected HMX, RDX, and TNT in all wells using all methods
 - Obtained complete data sets for each test method from wells MI058, MI669, MW-14S, MI404, and MI214
- Field Observations
 - Time to complete sampling varied greatly between methods
 - Limitations were documented for each method

Demonstration 1 MLAAP – Statistical Analysis of Results

- Analyzed data using Minitab® 15 Statistical Software Package
- Completed the following statistical analysis:
 - Graphical Analysis
 - Anderson-Darling (AD) Normality Test
 - Levene's Test for Equal Variances
 - Wilcoxon Test for Equal Medians
- Completed statistical analysis of the sampling times:
 - AD Normality Test
 - Analysis of sampling/pumping times using Analysis of Variance (ANOVA)

Demonstration 1 MLAAP – Statistical Analysis of the Analytical Results

- Graphical Analysis
 - Histograms and comparison of means and medians appeared to show non-normality
 - Standard deviations and variances appeared similar across the test methods
 - The AD and Levene's Tests were used to prove both assumptions from graphical analysis
- AD Normality Test
 - Majority of the distributions proved to be non-normal
- Levene's Test for Equal Variances
 - Selected due to the presence of non-normality
 - Results proved that the distributions for HMX, RDX, and 2,4,6 TNT for all four sample methods were not statistically significantly different
- Wilcoxon Test
 - Wilcoxon Nonparametric Test was selected due to the presence of non-normality
 - Results proved that the median results for HMX, RDX, and 2,4,6 TNT for all four sample methods were not statistically significantly different

Demonstration 1 MLAAP – Statistical Analysis of the Sampling Time Results

- Determined time data was normally distributed.
- Compared time data using an ANOVA.

Level	N	Mean	StDev
SNAP Sample	9	51.89	13.71
HS Sample Mins	6	22.00	7.43
InSTED Clark Pump	3	341.67	21.59
InSTED Masterflex Pump	4	58.00	4.76
EPA Sample Mins	3	134.00	13.89

Individual 95% CIs For Mean Based on Pooled StDev

Level	Lower CI	Upper CI
SNAP Sample	(*)	
HS Sample Mins	(*)	
InSTED Clark Pump		(*-)
InSTED Masterflex Pump	(-*)	
EPA Sample Mins		(*-)

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100 200 300 400

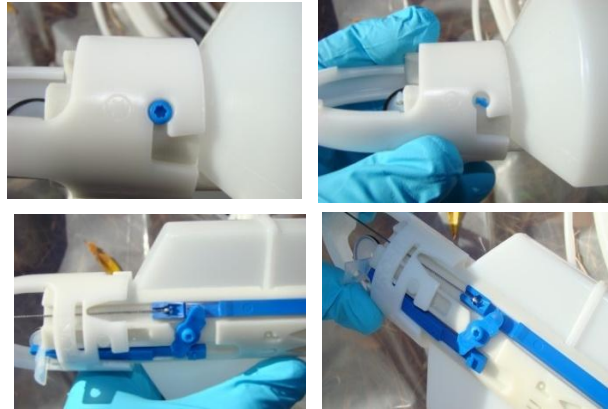
Pooled StDev = 12.58

Demonstration 1 MLAAP – Conclusions from Sampling Time ANOVA

- InSTED method with Clark pump yields a significantly longer sampling time than all of the other methods.
 - InSTED method was significantly faster using the Masterflex pump as opposed to the Clark pump
- U.S. EPA low-flow method requires a significantly longer sampling time than the sampling time for InSTED with Masterflex pump, HydraSleeve, and SNAP sample methods.
- SNAP and InSTED with the Masterflex pump methods yielded sampling times that were not statistically different.
- HydraSleeve sampling time is significantly less than the time required for of all the methods.

MLAAP Field Observations - Snap Sampler

- Snap Sampler® Limitations:
 - Ruggedness
 - Potential need for compressed air/electricity
 - Amount of equipment required in the field
 - Reliability
 - Ease of use



***Broken
Screw/Clips***



***Incomplete
Closing of Snap
bottle (1 of 28)***



Length of Sampler



***Tangled Air
Hose***



***Required
Equipment***

MLAAP Field Observations - HydraSleeve and InSTED

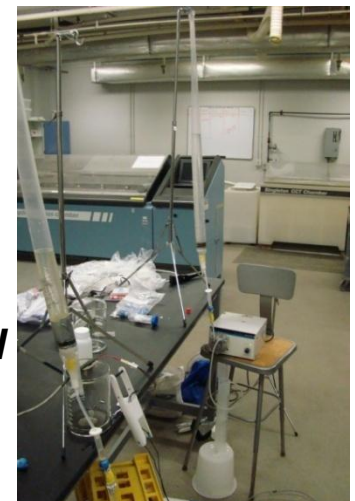
- HydraSleeve and InSTED sample sleeve limitations:
 - Ruggedness
 - Reliability
- InSTED extraction limitations:
 - In Situ extractions not possible
 - Time required
 - Expected 500 milliliters (mL) of the sample at a 10 mL/minute rate, anticipated to take approximately 50 minutes
 - Actual ranged from ½ mL/minute to 4 mL/minute resulting in extraction times of 4 to 8 hours



***Detachment at Reed Valve
Stem (Lost 1 sample out of 10)***



***Turbid Samples Increased
Extraction Time***



***Extractions Completed at
CTC's Laboratory***

MLAAP Field Observations – U.S. EPA Low Flow

- U.S. EPA Low-Flow limitations:
 - Extensive equipment required
 - Extensive sampling time (~ 2 hours)
 - Collection/Disposal of purge water required (~20 gallons/sample)



Collection of Purge Water



Monitoring Parameters and Collecting Sample

Demonstration 1 MLAAP – Conclusions

- Determined that the alternative methods are capable of providing analytical data for explosives that are not significantly different from data obtained using the U.S. EPA low-flow method (based on 5 sets of data obtained in this study)
- Determined that there is a significant difference between the time required to obtain a sample using the various methods
 - HydraSleeve – mean 22 minutes
 - Snap and InSTED (Masterflex) – mean 52 and 58 minutes respectively
 - U.S. EPA low-flow – mean 134 minutes
 - InSTED (Clark) – mean 342 minutes
- Identified limitations with the alternative technologies
 - Issues with collecting sufficient groundwater with Snap Sampler
 - InSTED use may be limited to specific contaminants of concern based on availability of SPE cartridges and analytical procedures

Demonstration 1 MLAAP – Conclusions (Cont'd)

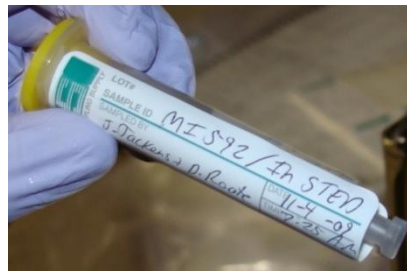
- Training is required to complete InSTED extractions.

- Spiking samples
- Extracting appropriate volume



- Identified areas of cost reduction with alternative *Spiking InSTED* technologies

- Less capital equipment required than for U.S. EPA
- Reduced labor
- Elimination of purge water disposal costs
- Reduction in sample volume with InSTED (~1,500 grams to 23)



***1 Liter Glass Amber Bottle
Compared to Cartridge***

Path Forward

- Demonstrate the alternative sampling technologies at the PAH site (April 2010)
- Develop User Guides for the InSTED and Snap Sampler
- Utilize data from the demonstrations to complete the evaluation of the effectiveness of the alternative sampling technologies at providing cost effective and scientifically defensible data



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